

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number  
**WO 01/40531 A1**

(51) International Patent Classification: C22F 1/047

Paul [US/US]: 31 Oakbrook Lane, Mineral Wells, WV 26150 (US). DUNBAR, Brady [US/US]: 143 Cherry Street, P.O. Box 468, Marienville, PA 16239-0468 (US).

(21) International Application Number: PCT/US00/16204

(22) International Filing Date: 14 June 2000 (14.06.2000)

(74) Agent: MCBEE, Susan, E., Shaw; Bowles Rice McDavid Graff & Love PLLC, 475 H Street, N.W., Suite 300, Washington, DC 20001 (US).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
PCT/IB99/02116 6 December 1999 (06.12.1999) IB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(71) Applicant (*for all designated States except US*):  
PECHINEY ROLLED PRODUCTS LLC [US/US]; 1 Willow Grove Mill Road, Ravenswood, WV 26164 (US).

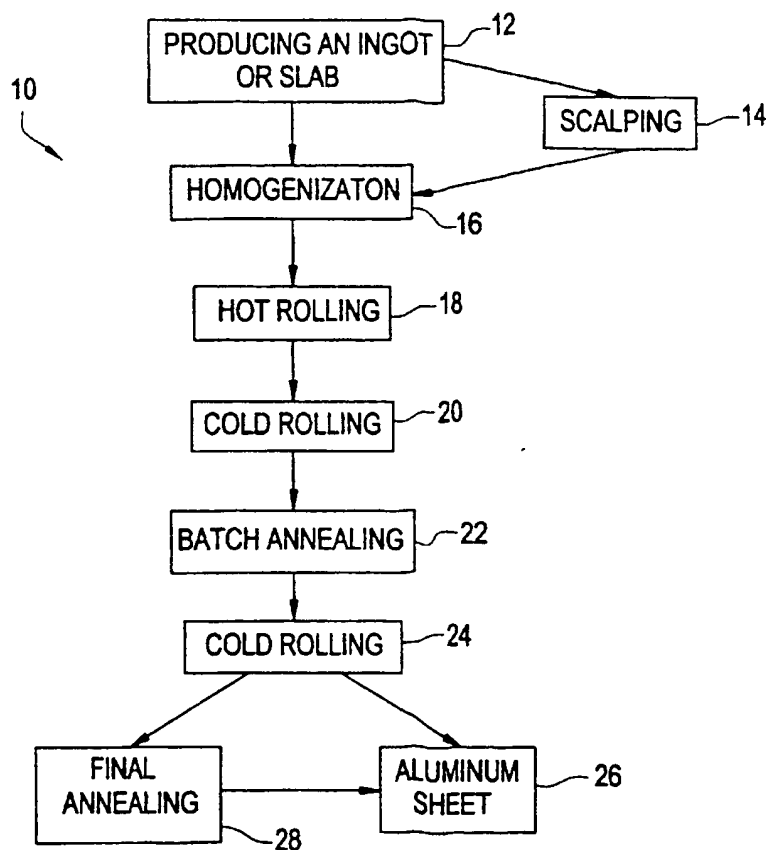
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): SMITH, Kenneth,

[Continued on next page]

(54) Title: HIGH STRENGTH ALUMINUM ALLOY SHEET AND PROCESS



(57) Abstract: Aluminum sheets and methods for manufacturing aluminum sheets are provided. The present invention involves control of processing conditions in order to achieve a fine grain size (i.e. ASTM rating of 8.5 or greater) in the material prior to a final cold working operation. Also included within the scope of the present invention are products having a fine grain size which have strength levels above what can be obtained in 5xxx alloys.

WO 01/40531 A1



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— *With international search report.*

## HIGH STRENGTH ALUMINUM ALLOY SHEET AND PROCESS

### Background of the Invention

#### Field of the Invention

5           The present invention relates to processes for making aluminum sheet and sheets made thereby, and more particularly relates to processes for making high strength, aluminum sheets including magnesium containing aluminum sheets and sheets made thereby involving batch annealing.

#### Description of Related Art

10           In conventional manufacturing processes for obtaining aluminum sheet, there is generally a trade off between the ultimate tensile strength, magnesium content and elongation of a material. For example increasing the cold work of the sheet generally results in increased ultimate tensile strength with a decrease in elongation. And as a further example, decreasing the cold work generally results in a decrease in ultimate tensile strength with a corresponding increase in  
15 elongation. Increasing magnesium content can improve the ultimate tensile strength of the alloy, but typically causes a corresponding increase in the cost of the alloy.

          As set out below, flash annealing processes have been developed to address some of the problems that have heretofore been associated with batch annealing, but flash annealing typically requires an additional handling step of unwinding and re-winding, whereas batch annealing does  
20 not require this additional handling.

          In contrast to the batch annealing process of the present invention, various flash annealing processes, also referred to as continuous annealing processes, have existed and require the additional step of continuously passing the sheet through a heating means as a single web to provide a heat up rate of the sheet at a greatly increased rate over that of batch annealing.

Examples of such flash annealing processes include Palmer et al. U.S. Patent 5,362,341, issued November 8, 1994, which is incorporated herein by reference; and additional continuous annealing processes are disclosed in Tanaka et al. U.S. Patent 5,062,901, issued November 5, 1991; Tanaka et al. U.S. Patent 5,240,522, issued August 31, 1993; Tanaka et al. U.S. Patent 5,496,356, issued November 6, 1990; Wyatt-Mair et al. U.S. Patent 5,470,405 issued November 28, 1995; Wyatt-Mair et al. U.S. Patent 5,496,423 issued March 5, 1996; Wyatt-Mair et al. U.S. Patent 5,514,228 issued May 7, 1996; Tahara et al. U.S. Patent 5,512,111 issued April 30, 1996; Shoji et al. U.S. Patent 5,518,558 issued May 21, 1996. Satou et al. U.S. Patent 5,578,114 issued November 26, 1996 involves a continuous casting process; Sanford et al. U.S. Patent 5,547,524 issued August 20, 1996 discloses a process for producing a structurally hardened plate involving heating opposite edges at various temperatures; Gen et al. U.S. Patent 5,616,189 issued April, 1997 discloses a process involving flash annealing; Bekki, et al. U.S. Patent 5,605,586 discloses a process involving flash annealing; Kamat U.S. patent 5,634,991 issued June 3, 1997 discloses a process involving annealing at the rate of heat up at 75 degrees per hour; all of which are incorporated herein by reference in their entireties.

The various flash annealing processes have typically required the additional step of unwinding and re-winding the coil of aluminum sheet. This winding is both time consuming and costly and the aluminum sheet can be damaged in the process, all of which add to the cost of the product. Batch annealing does not require that the aluminum sheet be unwound, and is thus very desirable. However, conventional batch processing has not obtained the desired combination of high ultimate tensile strength for a given level of elongation and magnesium level. For example, strength levels exceeding 448 MPa (65,000 psi) are currently not available in Al-Mg sheet products, as partially shown in the table provided below in the detailed description.

Consequently there is a need and a desire to provide a batch annealing process in the production of aluminum sheet which will provide a high ultimate tensile strength for a given level of elongation and magnesium level. There is also a desire to increase the ultimate tensile strength for a given magnesium level and the elongation percent in order to permit a reduced gauge

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/16204

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0506100 A	30-09-1992	JP 2059240 C	10-06-1996
		JP 5070904 A	23-03-1993
		JP 7094699 B	11-10-1995
		JP 5009680 A	19-01-1993
		DE 69204092 D	21-09-1995
		DE 69204092 T	25-01-1996
		US 5240522 A	31-08-1993
US 5480498 A	02-01-1996	NONE	
EP 0610006 A	10-08-1994	JP 7145441 A	06-06-1995
		CA 2114285 A	28-07-1994
		DE 69413571 D	05-11-1998
		DE 69413571 T	01-04-1999
		US 6056835 A	02-05-2000
		US 5573608 A	12-11-1996
WO 9711205 A	27-03-1997	US 5655593 A	12-08-1997
		US 5772799 A	30-06-1998
		US 5772802 A	30-06-1998
		US 5769972 A	23-06-1998
		AU 722391 B	03-08-2000
		AU 7362596 A	09-04-1997
		BR 9611416 A	23-02-1999
		CA 2232436 A	27-03-1997
		CN 1200771 A	02-12-1998
		EP 0851943 A	08-07-1998
		JP 11511389 T	05-10-1999
		US 5894879 A	20-04-1999
		US 6045632 A	04-04-2000

Figure 2B shows details of a grid circle of major stretch and minor stretch from Figure 2.

### Detailed Description of the Invention

The present invention is directed to methods and products wherein strength, formability, warm forming, SPF as well as other properties typically associated with aluminum sheet can be variously obtained depending on the process parameters utilized. These properties are important in various end use applications for aluminum sheet. For example, warm forming is often used in automotive body panels; SPF for aerospace applications. The use of an intermediate anneal with varying degrees of prior cold rolling is employed in aspects of the present invention to achieve desired final products. Materials of the present invention are particularly thought to be useful for any end product that employs low formability/high strength materials, for example, any materials for flat applications such as sign blanks, panels on transportation vehicles, and so on. Materials of the present invention have unexpectedly acceptable 4T bend properties for such a high strength material. In this regard, the prior art generally employs 5xxx alloys for similar end uses, but such 5xxx materials typically have Ultimate Tensile Strength (UTS) values less than 55-60,000psi. The present materials have UTS values which are higher than 5xxx alloys, but still retain or possess the desired formability requirements.

The processes of the present invention involve batch annealing and produce a sheet exhibiting a high level of ultimate tensile strength (i.e. for a given level of magnesium content and elongation). A typical process involves: (a) producing an aluminum ingot generally comprised of at least 3.0% by weight magnesium based on the total weight of the ingot (mass), (b) homogenizing the ingot, (c) hot rolling the ingot to produce a first intermediate product, (d) cold rolling the first intermediate product to produce a second intermediate product, (e) heat treating the second intermediate product to produce a third intermediate product, and (f) cold rolling the third intermediate product to produce the aluminum sheet. The sheet exhibits a relatively high ultimate tensile strength for a given level of magnesium and a given level of elongation.

A suitable process according to the present invention involves: (a) producing an aluminum ingot (mass) comprising of at least 2.0% by weight magnesium based on the total weight of the

ingot (mass), (b) homogenizing the ingot (mass) at a temperature of between 482°C-649°C (900°F and 1200°F), (c) hot rolling the ingot (mass) at a coiling temperature of between 288°C-382°C (550°F to 720°F) to produce a first intermediate product, (d) cold rolling the first intermediate product to produce a second intermediate product, (e) batch heat treating (annealing) the second intermediate product at a temperature of at least 316°C (600°F) to produce a third intermediate product, (f) cold rolling the third intermediate product to produce said aluminum sheet, and (g) optionally post processing the aluminum sheet by annealing the aluminum sheet at 93°C-382°C (200-720°F). The present invention provides the advantage of a relatively high ultimate tensile strength for a given level of elongation and magnesium thereby permitting higher performance of product for given applications. The high ultimate strength levels are achieved by cold working a fine grain microstructure which is developed in the annealing step (c) subsequent to a minimum of 50% cold working reduction in step (d). The annealing step may be batch annealing or strip annealing. The present process also allows for batch anneal to develop a fine grain microstructure without continuous annealing or flash annealing which typically involves unwinding of coils and additional effort.

An advantageous process according to the present invention is illustrated in Figure 1 which involves first producing an ingot (12) by the process (10) of the present invention. The ingot may also be referred to as a mass in the event that continuous casting is employed. In the event that an ingot is utilized, the ingot may need to be scalped (14) followed by or prior to preheating (16). After preheating, the product from the preheat step is hot rolled (18) followed by a minimum of 45% cold rolling (20). After cold rolling, the product is then subjected to batch annealing (heat treating) (22) and is then further cold rolled (24) to produce the aluminum sheet (26). The aluminum sheet can be post processed using a final annealing by heating the sheet to 93°C-382°C (200-720°F).

The alloy composition utilized for the ingot (mass) and the alloy sheet of the present invention has a magnesium level of at least 2%, for example 2 to 7% by weight based on the total weight of the composition (ingot, mass, sheet), more preferably a level of 3 to 6% by weight based on the total weight of the composition (ingot, mass, sheet). Supplemental alloy additions

in the composition preferably involve manganese at a level of 0.20 to 1.5 weight percent based on the total weight of the composition; silicon at a level of less than or equal to 0.3 weight percent based on the total weight of the composition; iron at a level of less than or equal to 0.4 weight percent based on the total weight of the composition; chromium present at a level of less than or equal to 0.25 weight percent based on the total weight of the composition; zinc present at a level of 1.8 weight percent or less based on the total weight of the composition; scandium present at a level of less than or equal to 0.5 weight percent; zirconium present at a level of less than or equal to 0.5 weight percent; with all other alloy additions being present at a level of less than or equal to 2 weight percent, and preferably all other ingredients being a level of less than 0.2 weight percent individually, with the balance of the composition generally being aluminum.

In a preferred process, an ingot of aluminum is produced by any technique known to one skilled in the art, and is scalped according to any known technique. The ingot (mass) is then preferably homogenized by raising the temperature of the ingot to the range of 482°C to 649°C (900°F to 1200°F) and generally holding the temperature within that range 482°C to 649°C (900-1200°F) for a time of less than or equal to 30 hours and preferably between 10 and 30 hours. The ingot (mass) temperature is then lowered to the range of 482°C to 538°C (900°F to 1000°F) and maintained within this range for a time period of at least one hour. Following preheat, the ingot (mass) is preferably hot rolled at a coiling temperature of between 293°C (560°F) and 360°C (680°F), or more broadly between 288°C (550°F) and 382°C (720°F), to produce a first intermediate product. The hot rolling can be done at any suitable temperature, however, it is desired that the hot rolling temperature be chosen so as to reduce or eliminate the possibility of recrystallization. A suitable initial thickness of the first intermediate product is for example 6.2 mm (0.25").

The first intermediate product is then cold rolled to produce a second intermediate product having a thickness of less than 50% of the thickness of the first intermediate product and more preferably less than 45% of its thickness, and preferably the cold rolling is done at a temperature of less than or equal to 204°C (400°F) to produce the second intermediate product. The second intermediate produce is then heat treated by batch annealing.



Batch annealing is accomplished by heating the entire wound coil of aluminum sheet as compared to flash annealing which involves annealing a single layer (web) of the sheet by unwinding the coil and annealing a particular portion of the sheet by passing the sheet through  
5 a heat treating station and then re-winding the coil. The present batch annealing avoids the requirement of having to unwind and re-wind the coil.

The annealing (batch annealing) according to the present invention occurs at a temperature of at least 304°C (580°F) and preferably above 315°C (600°F), and more preferably within the range of 332°C (630°F) and 371°C (700°F), for a period of at least two hours to produce a third  
10 intermediate product. This product has an average grain diameter of less than 19 microns (ASTM of 8.5 or greater number), for example a grain size of ASTM 11, or more broadly ASTM 8.5 to 12, and for example between ASTM 9 and 11 as measured by ASTM E112. The grain size of 8.5 corresponds to a grain size of about 18.9 microns, consequently, and the grain size are preferably less than 18.9 microns.

15 Following the batch annealing, the third intermediate product is cold rolled to produce an aluminum sheet having a thickness of from 20 to 80% (preferably 50 to 80%) of the thickness of the second intermediate sheet (a total reduction of 20 to 90%) to produce an aluminum sheet having an ultimate tensile strength of at least 380 MPa [55,000 pounds per square inch-(psi)] as measured by ASTM B557, and typically resulting in an ultimate tensile strength of between 414  
20 MPa (60,000 psi) and 686 MPa (85,000 psi), for example 510 MPa (74,000 psi), and having an elongation of between 4 and 7%.

The present invention also provides high strength alloys without the need for the addition of relatively expensive, excessive levels of strengthening additives, and without the need to impart significant cold work to the product to achieve the strength level. The reduced level of cold  
25 work needed to produce such high strength aluminum alloy is in part due to the very fast hardening rate exhibited by the batch annealed sheet (coil) of the present invention when compared with materials of the prior art.

Optionally, a final anneal at for example 93°C (200°F) to 382°C (382°F) for a time in excess of two hours may be utilized to further increase the formability of the sheet with some sacrifice in the tensile strength.

In more detail, the process for manufacturing an aluminum sheet comprises: (a) producing  
5 an aluminum ingot (mass) comprised of at least 2.0% by weight magnesium based on the total weight of the ingot, (b) homogenizing the ingot at a temperature of between 482°C (900°F) and 649°C (1200°F), (c) hot rolling the ingot at a coiling temperature of between 288°C (550°F) to 382°C (720°F) to produce a first intermediate product, (d) cold rolling the first intermediate product to produce a second intermediate product, (e) annealing the second intermediate product  
10 at a batch anneal temperature of at least 316°C (600°F) to produce a third intermediate product, and (f) cold rolling the third intermediate product to produce a fine grain aluminum sheet. Optionally a final anneal of the aluminum sheet may be performed to increase the elongation properties of the aluminum sheet by annealing the aluminum sheet at a temperature between 93 and 382°C (200 and 720°F). In particular, batch anneal of the second intermediate product  
15 produces a fine grain; cold working the fine grained material is what imparts substantial high strength properties which were not expected heretofore.

The present method produces an aluminum alloy sheet having 2% or greater magnesium with ultimate tensile strengths in excess of 380 MPa (55,000 psi). A fine grain size, specifically rating 8.5 or greater as measured by ASTM E112 prior to the final cold work is desirable in the  
20 processing method in order to enhance the strain hardening characteristics through increasing grain boundary area. Material produced by the present process may find suitable applications such as, but not limited to, flat sheet blanks, boat/ship stock (i.e. boat hulls, etc.), automotive brackets and structural applications.

A suitable chemical composition of material is as follows: no less than 2% by weight  
25 magnesium and no more than 6.0% by weight magnesium, no less than 0.20 weight percent manganese and no more than 1.5% by weight manganese, no more than 0.35 weight percent silicon, no more than 0.48 weight percent iron, no more than 0.25 weight percent chromium and

no more than 1.8 weight percent zinc; scandium present at a level of less than or equal to 0.5 weight percent; zirconium present at a level of less than or equal to 0.5 weight percent; with additional components each being less than 0.2 weight percent and then the balance being aluminum based on the total weight of the aluminum ingot.

5 In the preferred process, the ingots are scalped sufficiently to remove cast surface and ingots are prepared for hot rolling. The ingots are then homogenized by heating to a temperature range of 900°F to 1200°F (480°C to 648°C) and holding (maintaining) the ingots' temperature in this range for up to 30 hours, then cooling to 900°F to 1000°F (480°C to 537°C) and holding at that temperature for no less than 1 hour prior to hot rolling. The ingots may optionally be hot  
10 rolled without the final cooling step.

A suitable process involves, having the slabs hot rolled at a coiling temperature of no less than 299°C (570°F) and no greater than 360°C (720°F). The coils are then cold rolled to reduce the web thickness by at least 50%. After cold rolling, the coils are heat treated at a temperature of no less than 316°C (600°F) for at least 2 hours. During this heat treatment, the fine grains are  
15 nucleated, which provides for strengthening during subsequent cold rolling through increasing the strain hardening exponent (or aspect) of the material. The coils are then cold rolled at an additional 50 to 80% to make the final product thickness and take advantage of the increased grain boundary area created during the prior heat treatment.

The maximum strength levels obtained using the present process have generally not been  
20 achieved in prior batch processes and are not available in Aluminum-Magnesium sheet alloys. Conventionally, high strengths have been achieved through alloy additions and/or imparting significant cold work of the material with the resultant disadvantages as set out above. For example, an alloy having 4.6% Mg (by total weight) and 0.7-1.0% Mn, with 60% final cold work plus intermediate annealing at 132°C (270°F) for 2 hours according to the present inventive  
25 process has a 72 MPa ultimate strength level advantage over the same alloy (4.6% Mg and 0.7-1.0% Mn) cold rolled 80% made according to industry standard practice. (See Example 1 *infra*.) In another test (Example 2) a 5182 Alloy (commonly used for can lid stock) containing about

4.6% Mg and .38% Mn cold rolled about 63% according to the present inventive process has the same strength about 386-400 MPa (56.000-58.000 psi, Ultimate Tensile Strength) as the alloy has cold rolled 86% according to industry standard practice.

5 The following table shows some additional mechanical property limits of non-heat treatable alloys according to Aluminum Industry standards as described in Aluminum Standards and Data (ASD) 1997, published by The Aluminum Association (TAAI) and Tempers for Aluminum and Aluminum Alloy Products, February 1995, also published by TAAI. The values set forth herein represent standard strength and elongation properties for known 5xxx aluminum alloys.

TABLE I

Alloy and Temper	Specified Thickness inches (mm)	Tensile Strengths-MPa (KSI)				Elonga- tion (%)
		ULTIMATE		YIELD		
		(Min)	(Max)	(Min)	(Max)	
5086-H38	0.006-(0.15mm) 0.20-(0.5mm)	324 (47)		262 (38)		3
5154-H38	0.006-(0.15mm) 0.05 -(1.25mm)	310 (45)		241 (35)		3
5154-H38	0.051-(1.25mm) 0.113-(2.8mm)	310 (45)		241 (35)		4
5154-H38	0.114-(2.8mm) 0.128-(3.2mm)	310 (45)		241 (35)		5
5086-H18 (Sheet)	0.006-(0.15mm) 0.019-(0.47mm)	359 (52)	407 (59)	331 (48)		
5086-H19 (Sheet)	0.006-(0.15mm) 0.019-(0.47mm)			359 (52)		2
5086-H191 (Sheet)	0.006-(0.15mm) 0.019-(0.47mm)	373 (54)		345 (50)		2
5086-H39 (Sheet)	0.006-(0.15mm) 0.019-(0.47mm)	359 (52)		297 (43)		3

As a further step, a final anneal may be performed, the temperature range of the final

annealing will depend on the desired properties of the aluminum alloy. To enhance formability, the optional final anneal may be performed, for example, in the range from 93°C (200°F) to 380°C (720°F) for at least 2 hours. The temperature and time duration for the final anneal will be determined by the level of formability required for the final product.

- 5 Temperatures above 260°C (500°F) will typically be used for O temper products and applications requiring an extremely fine grain size, such as super-plastic-forming (SPF). These final anneals will generally reduce the ultimate tensile strength and yield while increasing the elongation.

The instant invention is further directed to methods of achieving very high tensile  
10 strengths, i.e. in excess of 55,000psi, with a non-heat treatable 5xxx alloy. Maximum strength levels (above 70ksi) obtained using this process are not currently available in 5xxx alloys. This type of very high strength material is particularly useful for applications where high strength or good dent resistance is important and where very little or no formability is required, such as for highway signs.

15

Conventional methods for producing high strength levels in 5xxx alloys generally involve addition of alloying elements, such as increasing Mg and/or Mn content and imparting significant cold work to the material. The present method involves control of processing conditions in order to achieve a fine grain size (i.e. ASTM rating of 8.5 or greater) in the  
20 material prior to a final cold working operation. Also included within the scope of the present invention are products produced according to such methods.

The development of the fine grain microstructure on the product prior to the final cold working operation is desirable, inter alia, since such a fine grain structure enhances the strain  
25 hardening characteristics of the material. In other words, with a fine grain size, the material strength increases more rapidly with cold work than a material with a large grain size.

A final annealing operation may be added for applications where some degree of formability is required. Administering a final annealing treatment will lower the strength of  
30 the product while concurrently increasing the elongation. However, when a material with very

high initial strength level is used i.e. above 55 ksi, the product following the annealing treatment has a very good combination of strength and formability versus 5xxx material currently available. This can be beneficial, for example, for use in applications where a 90 degree bend is being performed. Use of the present material would allow down-gauging for  
5 example (equal forming characteristics with higher strength versus conventional materials).

The following examples show the increased strength of alloys made according to the present invention. The present examples are intended to explain but not limit the present invention:

EXAMPLE 1.

- 10 Aluminum Alloy: (All percentages by weight)  
4.55% Magnesium  
0.98% Manganese  
0.01% Copper  
0.066% Silicon  
15 0.19% Iron  
0.10% Chromium  
up to 0.50% Scandium  
up to 0.50% Zirconium  
<2.0% All others  
20 Preheat according to the present invention and hot roll to a thickness of 7.25 mm (0.290") at a temperature of 343°C (650°F). Silicon is generally present as an unavoidable impurity in most industrial aluminum products. Silicon and iron are generally present in an amount of .40 maximum. The other trace elements that are not necessary to the present invention can be excluded if desired for any reason. This is true for all products according to the present  
25 invention.  
Process A (Prior Art Step). 80% cold roll aluminum alloy sheet, with no intermediate annealing.

Resulting Ultimate Tensile Strength: 438 MPa (63,500 psi)

OR

Process B. (According to Present Invention) Cold roll aluminum alloy sheet to 2.5 mm (0.100") (60% cold work) and anneal at 93-382°C (200-720°F) for 2 hours. Additional 60% cold roll to 1 mm (0.040").

5 Resulting Ultimate Tensile Strength: 510 MPa (74.000 psi)

The Example shows the alternative finishing steps for the alloy. The Process A, which was practiced in prior art methods, concludes with a cold rolling and no final anneal where it is shown that 80% cold work with no intermediate anneal results in an UTS of 438 MPa. Process B, according to the present invention, uses an intermediate or batch anneal after prior cold work to develop a fine grain size. Cold working the fine grain material an additional 60% obtains a material with an UTS of 510 Mpa.

As shown in the above example, completing the processing by 80% cold rolling the aluminum sheet to 80% of its thickness, with no intermediate annealing, results in a sheet having a Ultimate Tensile Strength (UTS) of about 438 MPa (63.500 psi). A sheet processed according to the current invention which has been 60% rolled and then annealed at 260-382°C (500-720°F) for 2 hours and cold rolled 60% again has a much higher UTS of 510 MPa (74.000 psi). This increased strength is significantly higher than a similar alloy processed according to prior art processes.

## 20 EXAMPLE 2 :

Aluminum Association alloy 5182 (commonly used for beverage can lids)  
[comparable to the composition of Example 1, except Manganese is 0.4%]

Process A (Prior Art Step): Preheat and hot roll mass as described in the detailed description. Hot roll sheet to 2.87 mm (0.115") at 332°C (630°F). Cold roll 86% to 0.4 mm (0.016").

25 Resulting Ultimate Tensile Strength: 386-400 MPa (56.000-58.000 psi)

OR

Process B: (According to the Present Invention) Same as Process A, but cold roll 62% to 1.1 mm (0.043") sheet thickness. Batch anneal sheet at 332°C (630°F)



Cold roll 63% to 0.4 mm (0.016")

Resulting Ultimate Tensile Strength: 386-400 MPa (56.000-58.000 psi)

Here again, an alloy sheet processed using a cold rolling step of 86% cold work following  
5 the hot rolling results in a UTS of 386-400 MPa (56.000-58.000 psi) for the alloy 5182 used for  
beverage can lids. The batch anneal of this process allows cold rolling to be used to roll the sheet  
to the final thickness of 0.4 mm (0.016") while maintaining the same UTS by increasing the  
formability of the alloy through annealing. That is, Process B, according to the present invention  
obtains the same strength level of 56,000-58,000 psi, with only 63% final cold work. In other  
10 words, much less final cold work is necessary or required to achieve the same properties and  
strength levels as the prior art.

### EXAMPLE 3 :

Same alloy as in example 1.

Preheat according to the invention and hot roll to a thickness of 7.25 mm (0.290") at a  
15 temperature of 343°C (650°F).

Process A (Prior Art) : 78% cold rolling with no final annealing.

Resulting UTS : 453 MPa (65.600 psi)

YS (60.400 psi)

Elongation 4.4 %

20 Process B (invention) : 55 % cold rolling and annealing at 132C° (270°F) for 2 hours,  
developing a fine grain structure.

Resulting UTS : 475 MPa (68.800 psi)

YS : 426 MPa (61.700 psi)

Elongation : 5.5%

25 The process which includes both a batch anneal and a final anneal provides a greater elongation  
over prior art and better mechanical resistance.

Process B shows a 5% increase in UTS and a 25% increase in in elongation of prior art  
Process A. As much as a 50% increase in UTS may be possible.

EXAMPLE 4 :

Same alloy and hot rolling as in example 3.

Process A 78% cold rolling with no final annealing. The cold rolled sheet is transformed  
 5 by superplastic forming (SPF)  
 Resulting SPF elongation : 375 %

Process B 55% cold rolling after annealing at 132°C for 2 hours to develop a fine grain  
 structure  
 Resulting SPF elongation : 375 %

10 The process of the invention provides the same SPF elongation with significantly less cold work.

EXAMPLE 5:

End Use: Sign Blanks (i.e. Highway Signs)

Produced according to Example 1

Current commercial standard material for sign blanks is 5052-H38,

15 Replacement with the instant product would allow significant  
 improvement in dent resistance and/or reduction in thickness.  
 Dent resistance is related to the product of the material yield  
 strength (YS) and the square root of the material thickness (T).

a. Increased Dent Resistance:

20 Current Commercial Product 5052-H38 yield strength is typically 32ksi  
 Typical Thickness = .080 inches

$$YS * T^{1/2} = 9.05 \text{ ksi} * \text{in}^{1/2}$$

Instant Product yield strength = 60ksi

For equivalent thickness of .080 inches

25  $YS * T^{1/2} = 16.97 \text{ ksi} * \text{in}^{1/2}$

This data confirms that there was an 87% increase in dent resistance at the same thickness  
 level here of 0.080". Large increases in dent resistance of the same scope shown here would be

expected in aluminum sheets of any thickness and could be calculated by those of skill in the art using known techniques. As is apparent by the formula, the increase in dent resistance would be related to the original thickness of the material.

b. Thickness (Weight) Reduction

5 To maintain a constant dent resistance; based on the product of the material yield strength and the square root of the material thickness:

10 A 5052-H38 sign blank product has a dent resistance of  $9.05 \text{ ksi} \cdot \text{in}^{1/2}$ ; replacing this material with the instant sign blank material at a  $YS = 60 \text{ ksi}$ , a thickness of  $.0227''$  could be used. Thus, there is a thickness reduction of 71.6%, while maintaining equivalent dent resistance.

EXAMPLE 6:

End Use: Improved Impact Energy (i.e. Tankers for Hauling Dangerous Goods)  
Priority according to Example 3 (%EL)

15 Instant product offers high value in terms of ultimate tensile strength (UTS) and percent elongation which are a factors used in determining the thickness requirements i.e. for tankers hauling dangerous goods.

When replacing steel with aluminum for such end uses, the following formula is typically used to determine the necessary aluminum thickness:

20

$$T_{st} = (21.4 \cdot T_{Al}) (UTS \cdot \%EL)^{1/3}$$

The following table compares the  $UTS \cdot \%EL$  for standard 5083 material produced with conventional methods (cold work) versus the instant product produced according to Example 3, but with two different final annealing temperatures.

Fabrication Method	Straight Cold Work	Fine Grain Roll (270°F)	Fine Grain Roll (400°F)
Product UTS	65.5 ksi	68.8 ksi	58.5 ksi
Product %El	4.4%	5.5%	8.1%
UTS * %El	288.2	378.4	473.85

#### 5 EXAMPLE 7:

Material produced via the instant method lends itself to obtaining a very good combination of high ductility and high strength in warm forming applications. Below is an example of a plain strain value from a forming limit diagram along with a corresponding minimum ultimate tensile strength value at a warm  
10 forming temperature of 250°C.

Forming Temperature = 250°C

Plane Strain = 100%

Minimum UTS = 40ksi

It is also possible to employ increasingly higher UTS values (i.e. 42ksi, 44ksi, 46ksi,  
15 48ksi, 50ksi, 52ksi, 54ksi, and even up to 60 ksi or higher).

As shown, for example, in Figure 2, grid circles etched onto sheets are analyzed after forming. Major and minor stretch values are measured according to circles shown. These vectors comprise a curve called a Forming Limit Diagram (FLD) shown at the bottom of Figure 2.

20 Strain paths which result below the curve are generally referred to by those of skill in the art as "safe" because they may be performed with no necking or fracture. "Above the curve" strain paths are avoided due to potential failure. In terms of formability, it is desirable for the curve to be shifted higher on the graph if possible.

Also shown in Figure 2 is an estimated room temperature curve for 5052 H32, as well as "plain strain" data points (at 0% minor stretch) for the material according to the present invention and 5052 H32 at 250°C. Plain strain is important to designers because it is the lowest point on the curve. Repeatedly the instant material's plain strain value is much larger than 5052H32 (100% vs. 70%) despite 5052 H32 elongation at room temperature being much higher (10% to 4%), for example.

The remainder of the FLD curve could be constructed according to known techniques and would be similar in shape to the curve shown in Figure 2.

#### EXAMPLE 8:

High strength (before warm forming) = 70ksi UTS  
 Plus  
 High Plain Strain Elongation during warm forming = 100% (as above)

This is versus a typical material 5052 H32 which has much higher room temperature elongation (i.e. 10% versus 4%) but much lower strength, about half (34ksi versus 70ksi). Thus, the instant product possesses are substantially higher (nearly 150%) strength and 50% of the room temperature RT elongation when compared with conventional materials such as 5052 H32, but has 100% warm forming plane strain value versus 5052 H32 warm forming plain strain value of about 70%. The UTS of 5052 H32 generally ranges from 31-38,000psi.

#### 5052-H32

UTS (room temp): 34ksi  
 %El (room temp): 10%  
 Plain Strain %Elg (250C): 70%

#### Inventive Material according to example 7:

US (room temp) 70ksi  
 %El (room temp) 4%  
 Plain Strain %El (250C): 100%

### CLAIMS

What is claimed:

1. A process for manufacturing an aluminum sheet, said process comprising:
  - (a) producing an aluminum ingot comprising at least 3.0% by weight magnesium based on the total weight of the ingot,
  - (b) homogenizing said ingot,
  - (c) hot rolling said ingot,
  - (d) cold rolling said first intermediate product to produce a second intermediate product,
  - (e) heat treating said second intermediate product, and
  - (f) cold rolling said third intermediate product to produce said aluminum sheet.
2. A process of claim 1, wherein said heat treating said second intermediate product includes batch annealing said intermediate product for at least two hours at a temperature of at least 316°C (600°F).
3. A process of claim 1, wherein said homogenizing comprises (i) increasing said ingot temperature to a temperature of between 538°C (1000°F) and 649°C (1200°F) for a period of between 10 hours and 30 hours and (ii) decreasing said ingot temperature to between 482°C (900°F) and 538°C (1000°F) and maintaining said temperature of 900-1000°F for at least one hour.
4. A process of claim 1, wherein said cold rolling of said first intermediate product results in the second intermediate product having a thickness of less than 50% of an initial

thickness of the said first intermediate product.

5. A process of claim 1, wherein said cold rolling of said third intermediate product results in said aluminum sheet having a thickness of 20 to 50% of a thickness of said third intermediate product.
6. A process of claim 1, further comprising a final annealing of the aluminum sheet.
7. A process of claim 6, wherein said final annealing is performed at a temperature of 93-382°C (200°F-720°F).
8. A process of claim 6, wherein said final annealing is performed at a temperature of 260-382°C (500°F-720°F).
9. An aluminum alloy sheet made by the process of claim 1.
10. A sheet of claim 9, wherein said sheet has a ultimate tensile strength of at least 380 MPa (55.000 psi) as measured by ASTM B557.
11. A sheet of claim 10, wherein said third intermediate product has a grain size of at least 8.5 as measured by ASTM E112.
12. An aluminum alloy sheet, said sheet comprising:
  - (a) from 3.0 to 6% by weight magnesium based on the total weight of the sheet, said sheet having an ultimate tensile strength of at least 380 MPa (55.000 psi) as measured by ASTM B557.
13. An aluminum alloy sheet, comprising:
  - (a) from 4.55 to 6% by weight magnesium based on the total weight of the sheet;
  - (b) at least 0.98% manganese by weight;

(c) less than 3% total by weight of other alloying element and/or impurities;  
said sheet having an ultimate tensile strength of at least 469 MPa (68,000 psi) as measured by ASTM B557.

14. An aluminum alloy sheet of claim 13, further comprising:

- (a) at least 0.066% by weight silicon;
- (b) at least 0.19% by weight iron;
- (c) 0.1% by weight chromium;
- (d) up to 0.50% by weight Scandium;
- (e) up to 0.50% by weight Zirconium; and
- (f) less than 2% by weight total of other alloying element and/or impurities.

15. A process according to claim 1, wherein said (b) is conducted at a temperature of between 482°C (900°F) and 649°C (1200°F).

16. A process according to claim 1, wherein said (c) is conducted at a temperature of between 550°F 720°F to produce a first intermediate product.

17. A process according to claim 1, wherein said (d) is conducted at a temperature of at least 316°C (600°F) to produce a third intermediate product.

18. An aluminum sheet material having a UTS of at least 55,000psi and having a room temperature formability which is substantially equivalent to a 5xxx alloy.

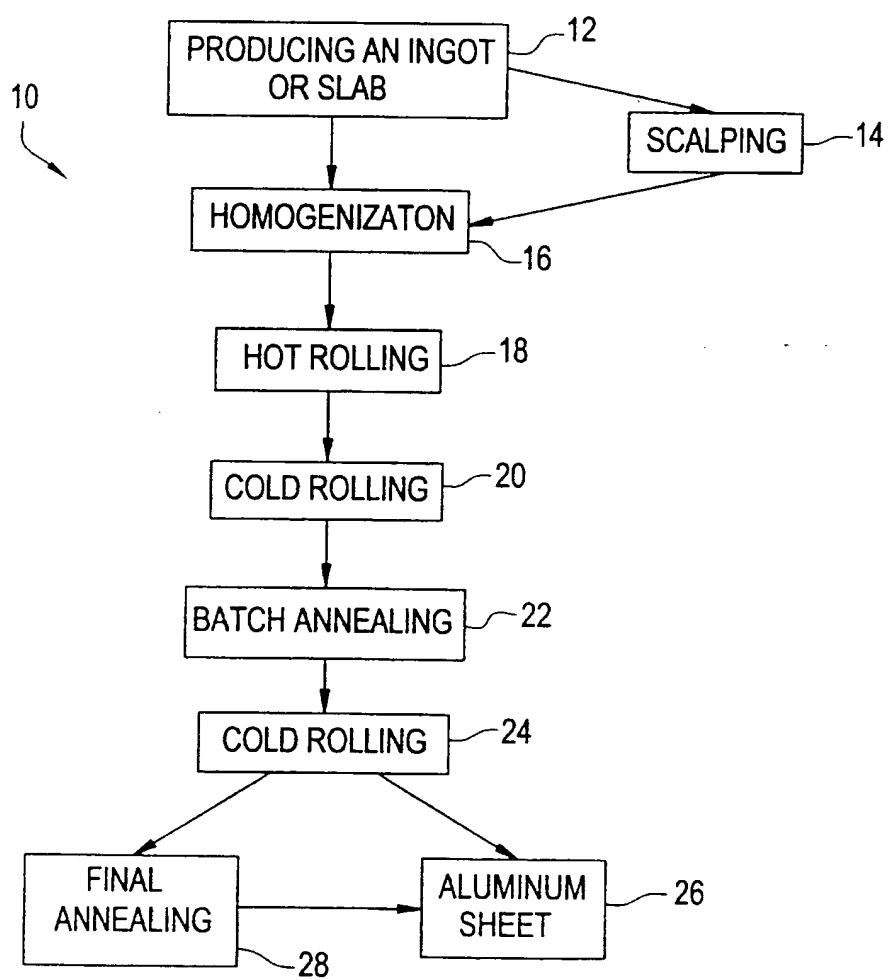
19. A method for increasing the strength properties of aluminum sheet, while maintaining room temperature formability comprising:

cold rolling said aluminum sheet to produce a product having a fine grain microstructure;  
conducting a batch anneal; and optionally  
conducting a final anneal.



20. A method for controlling the strength and/or room temperature formability of an aluminum sheet comprising:  
conducting an intermediate batch anneal of said sheet after prior cold rolling to form a fine grain microstructure to control the strength of said aluminum sheet; and  
if increased room temperature formability is desired, conducting a final anneal of said sheet after said prior cold rolling and said intermediate batch anneal.
21. An aluminum sheet prepared according to claim 20.
22. An aluminum alloy sheet, comprising:  
(a) from 4.55 to 6% by weight magnesium based on the total weight of the sheet;  
(b) at least 0.4 % manganese by weight;  
(c) less than 3% total by weight of other alloying element and/or impurities;  
said sheet having an ultimate tensile strength of 386-400 Mpa as measured by ASTM B557,  
wherein said sheet has been prepared using less than 86% cold work.
23. An aluminum hull structure formed from an aluminum sheet prepared according to the process set forth in claim 20.
24. An aluminum hull structure formed from an aluminum sheet prepared according to the process set forth in claim 1.
25. A sign blank made from an aluminum sheet according to claim 9, having a yield strength greater than 50 ksi and a dent resistance  $YS \cdot T^{1/2}$  greater than  $10 \text{ ksi} \cdot \text{in}^{1/2}$ .
26. A sign blank according to claim 25 wherein the dent resistance is greater than  $12 \text{ ksi} \cdot \text{in}^{1/2}$ .
27. An aluminum sheet material according to claim 13, having an SPF of more than 350%.

FIG.1



2/2

FIG.2

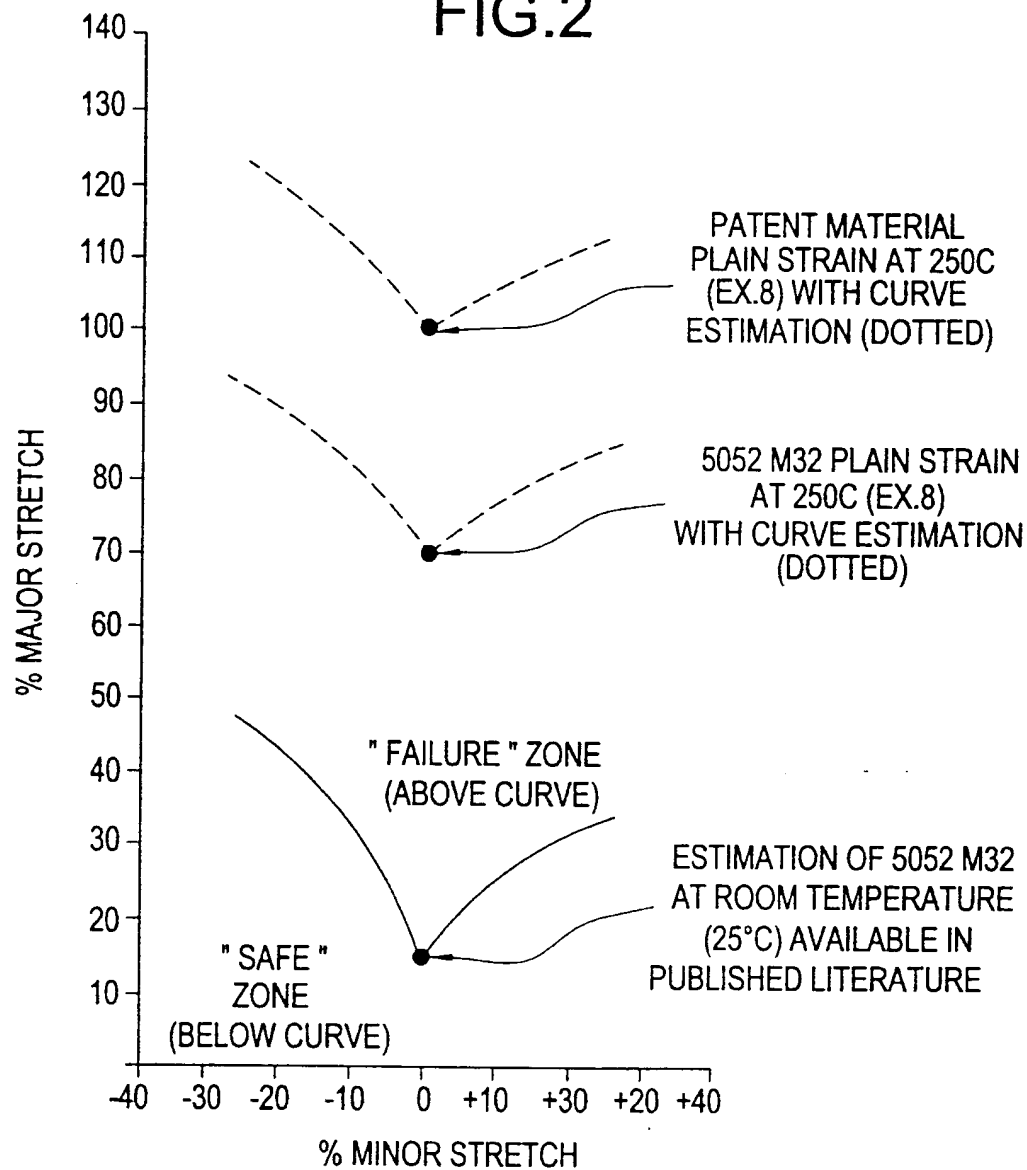


FIG.2A

GRID CIRCLES

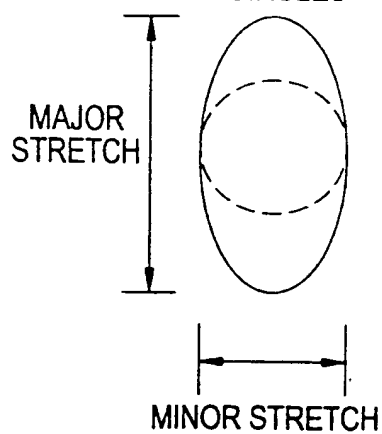
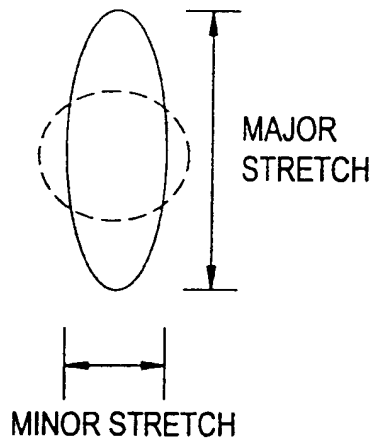


FIG.2B



SUBSTITUTE SHEET (RULE 26)

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/16204

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22F1/047

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 506 100 A (SUMITOMO LIGHT METAL IND) 30 September 1992 (1992-09-30) page 3, line 40 -page 4, line 53; claims 1,7; tables 1,8	1-27
X	US 5 480 498 A (BEAUDOIN ARMAND J ET AL) 2 January 1996 (1996-01-02) column 3, line 36 -column 5, paragraph 3; claim 1; figure 2	1,4-27
X	EP 0 610 006 A (TOYOTA MOTOR CO LTD) 10 August 1994 (1994-08-10) table 5	9-12,22
A	WO 97 11205 A (KAISER ALUMINIUM CHEM CORP ;SUN TYZH CHIANG (US); BETTS WILLIAM (U) 27 March 1997 (1997-03-27)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

10 October 2000

Date of mailing of the international search report

24/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Gregg, N

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/16204

1 017 05 007 10204

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0506100	A	30-09-1992	JP 2059240 C	10-06-1996
			JP 5070904 A	23-03-1993
			JP 7094699 B	11-10-1995
			JP 5009680 A	19-01-1993
			DE 69204092 D	21-09-1995
			DE 69204092 T	25-01-1996
			US 5240522 A	31-08-1993
US 5480498	A	02-01-1996	NONE	
EP 0610006	A	10-08-1994	JP 7145441 A	06-06-1995
			CA 2114285 A	28-07-1994
			DE 69413571 D	05-11-1998
			DE 69413571 T	01-04-1999
			US 6056835 A	02-05-2000
			US 5573608 A	12-11-1996
WO 9711205	A	27-03-1997	US 5655593 A	12-08-1997
			US 5772799 A	30-06-1998
			US 5772802 A	30-06-1998
			US 5769972 A	23-06-1998
			AU 722391 B	03-08-2000
			AU 7362596 A	09-04-1997
			BR 9611416 A	23-02-1999
			CA 2232436 A	27-03-1997
			CN 1200771 A	02-12-1998
			EP 0851943 A	08-07-1998
			JP 11511389 T	05-10-1999
			US 5894879 A	20-04-1999
			US 6045632 A	04-04-2000